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Shape resonances in vibrational excitation of molecules : [100] symmetric stretch mode excitation in CO₂

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Résumé. — La section efficace différentielle d'excitation vibrationnelle résonnante du mode d'élongation symétrique [100] de CO₂ est obtenue entre 1 et 35 eV. A côté de la résonance de forme bien connue de symétrie π_u et centrée à 3,8 eV, on observe deux nouvelles structures résonnantes très larges et de faible intensité. Ces structures centrées respectivement à 10,8 eV et 30 eV sont attribuées à des résonances de forme de symétrie σ_g et σ_u prévues par de récents calculs théoriques de Dehmer et Dill utilisant la méthode de diffusion multiple.

Abstract. — The differential cross-section for vibrational excitation of the [100] symmetric stretch mode in CO₂ is obtained in the 1-35 eV energy range. Besides the well known π_u shape resonance at 3.8 eV, two new resonance structures with low intensities and large widths are observed. These structures centred at 10.8 and 30 eV are attributed to σ_g and σ_u shape resonances respectively, as predicted by theoretical continuum multiple-scattering calculations by Dehmer and Dill.

1. **Introduction.** — Shape resonances are well known for the enhancement of vibrational excitation cross-sections at low energy (0-5 eV) [1]. These resonances are observed in electron scattering when the interaction potential between the incident electron and a molecule produces a centrifugal barrier resulting from the balance between centrifugal and electrostatic forces. The electron is trapped behind the centrifugal barrier to produce a short-lived negative ion, and escapes by tunneling through the barrier. Recently the role of centrifugal barriers has been shown, both theoretically [2, 3] and experimentally [4, 5] to be dominant in the excitation of inner-shell electrons to discrete states and in photoionization [3].

A continuum multiple-scattering approach to electron molecule scattering [3] predicts the existence of broad shape resonances characterized by phaseshift increasing by less than π radians over several volts at high energies (10-50 eV). These very short-lived resonances are difficult to observe in elastic and total cross-sections because of the presence of the dominant direct process. But they can be observed in vibrational excitation cross-section as the direct process is practically not observed at high energies [3].

2. **Experimental method.** — We have used an electron spectrometer made of two electrostatic filters to measure differential cross-sections in electron scattering after interaction with a target gas beam crossing the incident electron beam at right angles. This apparatus has been already used for resonant vibrational excitation in NO [6], CO₂ [7] and SO₂ [8] at low energies. The overall resolution was 50 meV, so that the first fundamental vibrational modes in CO₂ were resolved. The energy scale of figure 1 was obtained by observing the $1s\ 2p^2\ ^2S$ resonance in the elastic scattering of helium at 19.36 eV in a CO₂ + He

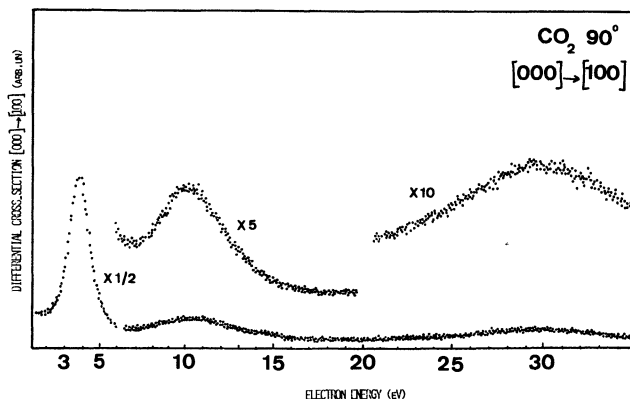


Fig. 1. — Differential cross-section for vibrational excitation of the [100] symmetric stretch mode in CO₂ observed at 90°.

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mixture. Because of the large energy range, the transmission of electrostatic optics has been calibrated with absolute elastic cross-sections in helium [9, 10] between 4 and 35 eV and for scattering angles from 30 to 120°.

3. Results. — Figure 1 shows the differential cross-section for exciting the vibrational mode [100] (symmetric stretch) in CO₂ between 1 and 35 eV for an angle of observation of 90°.

The intense peak at 3.8 eV was recently studied in detail by Čadež and collaborators [7]. They observed oscillatory structure whose position moves towards higher energies, and whose relative intensity increases when observed in higher vibrational levels. These structures are related to the autodetaching width of the resonance being of the same order of magnitude as the separation between vibrational levels. They can be described as an interference pattern between the nuclear wavefunction and a single reflected wave on the potential barrier (boomerang model) [11]. This resonance is characterized by a dominant $l = 1$ partial wave, with a small contribution of the $l = 3$ wave which is observed to decrease throughout the resonance energy region [13]. Above 4.4 eV this resonance is observed in the dissociative attachment process giving O⁻ [12] in competition with the autodetaching process.

The broad bump centred at 10.8 eV in figure 1 is attributed to a σ_g shape resonance. The width of 5 eV (Table I) gives a lifetime as short as 1.3×10^{-16} s. This resonance was observed in excitation of the [200] vibrational mode with an intensity 5 times lower, but it cannot clearly be observed neither in the elastic cross-section, presumably because of the dominant direct process, nor in the cross-section of the bending mode [010] presumably because of its very short-lived nature. The theoretical calculations [3, 13] predict the $l = 2$ and $l = 4$ partial waves to be dominant, but with varying contribution in the resonance region as reflected in the angular distribution [15] of the [100] excitation mode. A discrepancy of 2 eV is observed between the theoretical and experimental positions of the resonance, but it seems that the theoretical position is sensitive to the exchange approximation [14] especially at low energy.

The low intensity bump at 30 eV is attributed to a σ_u shape resonance. The position is in good agreement with theoretical prediction [3, 13]. The resonance is observed in the cross-section for exciting the [200]

vibrational mode with an intensity 7 times smaller than for the [100]. In table I we notice that when the width of the resonances increases the ratio of the cross-sections $v = 2/v = 1$ decreases as expected for short-lived resonances, and this supports the attribution of the 10.8 and 30 eV cross-section enhancement to broad resonances rather than to the existence of a number of overlapping resonances. Further evidence for the existence of these resonances can be provided by inner-shell photoionization spectra [3], and the two broad features observed at ~ 6.5 and 17 eV above threshold in the carbon K-shell photoionization spectrum of CO₂ [17] can be due to the same σ_g and σ_u shape resonances. The eigenphase calculations [13] predict that the $l = 1, 3, 5$ partial waves contribute to the σ_u resonance. But the angular distribution of the electron having excited the [100] level in the σ_u resonance energy does not allow the mixture of these three partial waves to be determined because the number of parameter is too high for the fitting procedure to have any physical significance [15].

The multiple scattering approach [3] predicts δ_g and δ_u shape resonances, but they are low intensities and are not observed in vibrational excitation, being weakly coupled with nuclear motion as they are not oriented along the molecular axis.

4. Conclusion. — Two new short-lived shape resonances have been observed in the vibrational excitation in CO₂. The existence of such high energy shape resonances appears as a common phenomena in molecules and has already been observed in N₂ [16, 14], in CO [15] and is being looked for in diatomic molecules NO, O₂ and HCl and in polyatomic molecules COS, BF₃ and SF₆.

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Table I. — *Properties of shape resonances in CO₂.*

Energy position	Symmetry	Half-width (eV)	$\frac{[100]}{[200]}$ ratio
3.8	π_u	1.2	1.8
10.8	σ_g	5	5
30	σ_u	8	7